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PROBLEMS OF THE CHLORINE INDUSTRY IN THE FOURTH FIVE YEAR-PLAN

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Among problems of a technical nature which require solution in the chlorine industry during the fourth Five-Year Plan, the problem of the methods of chlorine production is of the utmost importance. Not only must the requisite amount be produced, but chlorine must be produced by a more modern method, insuring a simplification of the process. It must be cheaper and a high-grade product.

Selection of technical methods of production in the chlorine industry is not as simple as in the soda industry where the one and the same method has predominated for many years. Electrolysis methods in the chlorine industry are constantly being improved. It is clear from this that we cannot limit ourselves during the current Five-Year Plan to methods in use today, which are by no means poor but which are not based on the use of the diaphragm. It will also be necessary to devote attention to the mercury method of electrolysis and to utilize the highly concentrated and pure alkali obtained in this manner for the storage-battery industry, the artificial-silk industry, etc. We believe that in the next few years it will be possible to carry out in good time the recommendations made by our specialists a long time ago to have in the Soviet Union several installations based on the mercury method. It is true that the mercury method in use today has two systems, the horizontal and the vertical. Which of the two systems should be selected? Some of our specialists are definitely prejudiced against the vertical system. We think, however, that it is more expedient to follow both courses.

When constructing new mercury cells with a horizontal cathode, it is essential to incorporate the principle of building them from separate, less cumbersome elements (frame- or collapsible-type cells). New disk-shaped mercury cells should be constructed using less volume of mercury. Construction of mercury cells with a nonrotating vertical cathode so far can be only of an

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experimental value.

The incorporation of the mercury method brings up the question of combining this method, based on the use of amalgam, with other processes, chiefly on a smaller scale. Some processes, however, in the event of their success, may have great technical importance. The problems of recovering mercury for maximum economy in production likewise must not be disregarded.

It does not follow, however, that methods based on the diaphragm should not be made more efficient. Here, too, new procedures must be put into practice along the lines of intensification, mechanization, and modernization, as well as in the improvement of the diaphragm. Future improvements are even feasible in such widely-used cells as the cylinder cells, for example. In the USA and England, there are a number of types of this cell. Two enterprises in the USA are using modified Hooker-Windecker cells for electolysis installations. Other modifications of the cylinder cell are entirely possible.

A fruitful field of endeavor along these lines lies before designers and research workers.

The above-mentioned measures will raise the equipment of the most important shops of the chlorine industry to a high technical level, reduce capital expenditures, improve operating efficiency, and raise the quality of the finished product.

Conditions under which electric power is supplied play a very important role in the success of electrolysis of the chlorine industry. Direct-current electric power is naturally of prime importance. However, the problem of charging cells with direct current becomes increasingly difficult with increased loading of chlorine cells. If we select a D.C. voltage of 150-270 v to charge modern cells which have a load capacity of 12,000-15,000 amp, we will be unable to use mercury rectifiers. If 700-800 v are selected, we can use mercury rectifiers, but we must use such a large number of cells (180) in the circuit that the lines may be overloaded. Future enlargement of the basic equipment in the chlorine industry (electrolytic cells) should be carried out slowly and only in accordance with the general increase in the demand for chlorine and the power potential of the country. Currently the incorporation of even a few horizontal or disk-shaped cells with a load capacity of 24,000 amperes may present a serious problem to electricians. But 24,000 amp are the limit to the loading capacity only of horizontal mercury cells. Disk-shaped cells may be loaded up to 40,000 amp. An installation with only one bank of such cells using 270 v in the circuit will have the capacity to produce over 20,000 tons of chlorine annually but will require the installation of a complex converter substation with massive motor generators. If the voltage of the circuit is 700 v and the cells are charged from mercury rectifiers, the production capacity of a single bank will be approximately 80,000 tons annually, but it will be hardly feasible to ground it in one spot. When designing equipment with unusually large electric parameters for our chlorine enterprises, it is necessary for the electricians of the chlorine industry to work closely with specialists of the power industry and prepare a number of drafts and models of appropriate machines and rectifiers. Electricians must also plan for the use of a new-type converter, the so-called contact rectifier, which transforms alternating current into direct current and which will give the chlorine industry a timely combination of tremendous load capacity of circuits, moderate voltage (150), and high efficiency.

Concerning raw material used in producing chlorine by the electric method, it has become necessary to supply each enterprise with raw material from a definite deposit in order to avoid subjecting the brine-purification system to fluctuation.

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Considerable efficiency is needed when establishing salt warehouses. First of all, it is necessary to mechanize the unloading of freight cars (with booms, grab buckets, pneumatics); secondly, any secondary transference of salt from warehouse to the plant should be avoided. Salt should be dissolved at the warehouse by direct washing with water or by electrolyte. For this purpose, open-platform warehouses with specially constructed floors (cemented, finished with tiles) may be used, as well as closed contiguous vertical bunkers serviced from above by conveyers. For dissolving salt it is expedient to use water from pressure condensers of the evaporating plant. When using the mercury method, a thermal balance in circulating brine must be established so that the loss of heat in the electrolyte on its way from the cells to the warehouse for resaturation and through the purifying station would correspond to the amount of heat regained by the brine in the electrolytic process.

A great deal more attention than has been given heretofore must be paid to the problem of purifying brine. The concept that one of the features of the mercury method is the absence of a need for brine purification is false. Electrolytic methods which use the diaphragm as well as the mercury cathode always require the most careful purification of brine. Purified brine for diaphragm cells should not contain more than 15 mg of calcium per liter, and not more than 4-5 mg of calcium per liter for mercury-cathode cells. Magnesium should not be in excess of 5 mg per liter for diaphragm cells, while the presence of magnesium in mercury-cathode cells is inadmissible. In addition to this, special attention should be paid to the fact that brine must be entirely clear. A continuous method purification may be resorted to for diaphragm cells. For mercury-cathode cells, which require special care in purification, it is more expedient to adopt the "staggered" method of purification, in which the continuous output of brine takes place as a result of alternate carrying out of an intermittent purification process in each of three tanks.

Despite the fact that prolonged standing of brine after purification is practiced in the existing chlorine enterprises, it has been recognized that filtration of brine is necessary.

With respect to the content of sulphate ions in purified brine, not more that 2-3 gr per liter should be allowed, otherwise purification with barium salts becomes necessary.

When incorporating the mercury method of electrolysis, a method of dechlorination must be adopted prior to resaturating the impoverished anolyte. In this connection a physical method has been introduced into the industry, which is based on the removal of chlorine from the anolyte by vacuum. Besides this, there is another method of dechlorination whereby the anolyte is allowed to pass through a layer of waste graphite anodes. The latter method is more suitable for us. It is necessary to bear in mind the fact that this method is simpler to adopt but requires more careful control. It should be taken into consideration that in the first method the chlorine that has been drawn off is directed into a common receptacle, while in the second method there is waste of chlorine (approximately 1 percent).

With respect to electrolysis plants, our problems boil down to elevating to a high technical level the maintenance and operation of equipment. The electrolysis room must sparkle with clean cells, pipes, pumps, motors, storage tanks and auxiliary equipment. First of all the cells proper and chlorine pipes must be absolutely gas-tight and all liquid conductors must be in perfect condition. Repair crews must be responsible for maintaining cells in a gastight condition. It is unthinkable to maintain chlorine equipment in condition without maintaining an adequately large machine shop for timely fulfillment of emergency, preventive maintenance, repairs. However, this is not the entire problem.

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Skillful service operations, proper organization of such operations, and the degree to which a plant is equipped with necessary instruments and appliances for checking, regulation, and automatic adjustment plays a substantial role.

While placing before the personnel of the chlorine industry the task of raising the level of electrolysis equipment maintenance, it is nevertheless necessary to require the planning organizations and the administration to pay more attention to these problems. Shops are far from identical. Shops producing chlorine cannot be built as low and with such a small cubic content as other hazardless shops. As a rule, there should not be any odor of chlorine in the electrolysis rooms. A supply of air is necessary as a means for air conditioning the electrolysis room in the event of accidental or momentary disruptions. The electrolysis room should be high and wide, with lighting obtained through wide windows which easily open out into the street, and with glass doors. This care and cleanliness also applies to auxiliary buildings.

In connection with basic equipment—the cells—used in electrolysis, a system should be established throughout whereby each cell would have a number and its own card in the senior foreman's card file, wherein the condition of the cell would be indicated. This is very important for checking and testing. Application of anticorrosion paint and constant repainting should be made a regular practice in electrolysis. The more orderly and cleaner the electrolysis room, the less chance of production losses and leakage in the current. This is especially important in the presence of a voltage of 500-800 v in the electrolysis circuit.

A great deal of attention must be paid to supplying the chlorine industry with graphite anodes. In connection with the drop in the production of the main electrode plant, the organization of anode production in a new plant must be carried out efficiently and speedily. We are confronted on the one hand, with the problem of promoting the most rapid implementation of acquired experience in the new electrode plant and, on the other, of introducing, through research and experimental work, new measures which are vital for bringing the quality of anodes up to the required perfection. In such a complicated process as the production of graphite anodes only the simultaneous work of specialists of the chlorine industry and specialists of the electrode profession can bring about the final formulation of new techniques for producing anodes for the chlorine industry.

Concerning the problem of asbestos diaphragm for cells, it is essential henceforth that Soyuzasbest [Union Asbestos Industry] be enabled to produce type "I" asbestos for the needs of the chlorine industry. Apart from this, the Asbotekhnika Trust must succeed in improving its technological process of paper production. If these technical improvements at the given enterprise are not feasible due to technical reasons, production of asbestos paper for the chlorine industry must be turned over to another enterprise. We do not believe that it is expedient for the Ministry of Chemical Industry to have control of the production of asbestos paper. There is no need in encumbering the chlorine industry with the execution of immediate assignments pertaining to the paper industry.

It is true that the future use of Hooker-type cells with a molded asbestos diaphragm is not to be excluded, but this does not solve the problem regarding the quality of asbestos paper for other plants.

With respect to work in the field of cathodes for the chlorine industry, reduction of the cathode potential and selection of suitable materials and shapes for cathodes may be considered important among the immediate problems. The problem of perfecting anode clamps and reducing voltage loss in these connections is already being worked on. The remaining problem entails bringing

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the experiments to a conclusion and putting them into wide practice. Mastering the method of copper plating anode electrodes at points where current-conducting busbars are attached is also of interest. A method should also be worked out in the impregnation of graphite-anode electrodes so that the impregnating substance would pass under pressure from the center of the electrode to its outer surface.

Previously we mentioned the problem of gastight cells and pipes in electrolysis. Such leakproof measures may be maintained up to certain physical limits. When the equilibrium between generation and take-off in the chlorine plant is upset, the pressure of chlorine in electrolysis may rise to such heights that leakage of gas will occur. A definite step should be taken to introduce automatic regulators which would insure automatic reversal of the flow of a portion of chlorine into an absorption apparatus when the pressure exceeds the normal limits. Experience has shown that in such cases it is more expedient to "destroy" (absorption by alkali) some of the chlorine rather than to subject the established system of electrolysis to fluctuation. Actually no "destruction" of chlorine takes place, since under proper planning the excess bleaching liquid that is obtained in these instances may be used for bleaching or sanitation purposes. At any rate, from the point of view of the electrolysis system, accident prevention and sanitation will make a considerable gain.

In the field of chlorine condensation there is the problem of continuing with the conversion of surface and sprinkler chlorine condensers to compound condensers. Inconveniences encountered with the latter in respect to channelling chlorinated water into pipes must be removed by having this water return to mixing towers after it has been passed through intermediate condensers.

There is nothing new in the process of drying chlorine. It is merely necessary to introduce improved methods of distributing (spraying) sulfuric acid inside the drying towers and to perfect the construction of the towers by covering the inside of the towers with film of chlorovinyl resins.

In transporting chlorine the problem has arisen of the chlorine changing into a nonliquid state due to use of multistage pumps.

When adopting the mercury method, one must take into account the presence of a somewhat larger amount of hydrogen in the chlorine than in methods in which the diaphragm is used. When liquifying such chlorine, it is necessary to work at lowered coefficients of liquifaction in order to avoid excessive concentration of hydrogen in the waste gas. These conditions must be considered when planning appropriate installations for liquifaction. In electrolysis, the presence of hydrogen in the chlorine in mercury cells should not cause any complications if proper attention is paid to cells when they are being filled.

When using mercury cells, special attention must be paid to the way in which mercury is handled, since the loss of this very valuable metal may severely affect the entire economy of chlorine production. A considerable amount of mercury is carried off in waste materials from the hydrogen demuders. Depending upon the future purpose of this hydrogen, some sort of method should be selected to remove the mercury from it. If, for example, dry hydrogen is necessary in order to obtain dry hydrogen chloride, a method of super-cooling must be selected to remove mercury, even if this method is complex and costly. If hydrogen requires the usual moisture, then in order to remove mercury the chemical method (nonchlorine anolyte) of absorbing mercury may be used to a certain degree. Further cleaning and recovery of reaction products by means of activated charcoal is necessary.

In modern technology, hydrogen is a very valuable product and has varied uses. That is why chlorine industries should strive to use every cubic meter

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of hydrogen. The latter is used in welding, in laboratories, and in various hydrogenation processes in organic chemistry. The degree to which the plan for the use of electrolytic hydrogen should be worked out in detail depends upon the degree to which the balance of chlorine is being worked out in detail in chlorine industries. When planning chlorine enterprises, utilization of the entire chlorine and hydrogen produced must be foreseen. Experience has shown that proper utilization of hydrogen may effect favorably the thermal and financial balance of a chlorine enterprise. Chlorine plants must be provided with hydrogen gas tanks and compressor stations. The ensuing expenses may be well worth it.

Concerning liquid chlorine, there is the problem of increasing the production. When handling compressed chlorine, the safeguarding of an installation with reinforcing materials (graphite lining) and equipment (chiefly fittings) for the timely fulfillment of maintenances, preventive maintenance, and capital repairs has special significance. A guaranteed supply of containers and a steady market are also very important. In addition to this, it is important to thoroughly analyze the advantages and disadvantages of the methods of liquifying chlorine through deep refrigeration with and without the presence of compressors, as well as the method of liquifaction under high pressure and water cooling, and to select one or the other method for the future. The intoduction of chlorine gas tanks is awaiting its turn. More machinery for preparing containers should be worked out for large liquifying plants.

In the field of chlorine bleaching-compound production, practically speaking, the most useful is the production of a high-grade stable product if production of bleaching or disinfecting chlorine in the form of a bleaching powder is to be continued. Nevertheless, the bulk of bleaching chlorine must be delivered as liquid chlorine, especially to large cellulose enterprises. In the production of the bleaching powder, the installations concerned are faced with the problem of searching for new equipment which would be lighter and more modern than the Bakman chambers. Also of interest is the use of compact apparatus in the shape of horizontal revolving and nonrevolving drums or apparatus in the shape of small mechanized chambers with high output capacity.

The industry faces the problem of ultimately mastering the technology of producing high-grade, solid hypochlorite. The possible scales on which it can be produced is still not clear. It is a fallacy to think that substitution of bleaching powder with such a fine product is imminent. Its conjuncture with chlorite also is not clear.

The problem of the production of chlorates is somewhat complex. When selecting a method of production it is important to take into account the demand for both chlorine and alkali. The chemical process has the advantage in that a good portion of electrolytic chlorine is absorbed. In addition, alkali, a product which is valuable for the market, is left over as waste. When the use of caustic alkali is necessary in certain installations, the chemical method of chlorate production has the above-mentioned advantages over the electrolytic method. If there is a shortage of chlorine and there is no acute need for the production of alkali (if there is in reserve a large supply of caustic alkali in soda enterprises), the electrolytic method has the advantage in chlorate production. In this instance, in addition to the main product, chlorates, hydrogen will be obtained as waste.

Urgent problems in the production of synthetic hydrochloric acid include only the mastering of working with low-grade chlorine, methods of purification from bromine, and utilization of new materials, especially graphite, when producing equipment for condensing the gas. The problems of liquification of hydrogen chloride remains unsolved. One should take into consideration that a considerable amount of hydrochloric acid will be

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obtained as a secondary product when producing organic products. In isolated cases the following question may arise: which will be more economic at the time, to produce chlorine at the required rate and sell the waste hydrochloric acid in the market, to reprocess the hydrochloric acid obtained as waste back into chlorine and hydrogen by the electrolytic method, or, perhaps, to oxidize chlorine in furnaces by a chemical process? Preliminary processing of both methods in the dissociation of hydrochloric acid may be of interest in the future.

The need for taking on production of ferric chloride, aluminum chloride, and a number of other inorganic chlorine compounds is obvious in itself.

Concerning the third product of electrolysis — alkali (caustic soda or caustic potash) — we are faced with problems in technology as well as in the types and quality of products.

In connection with the technology of reprocessing alkalies obtained in diaphragm cells, the problems chiefly center around the evaporation process wherein a broader application of the centrifuge for separating salt is necessary. In connection with this, the system of cleaning the salt must be made more efficient. This should reduce the amount of washing water and subsequently the consumption of vapor in the evaporating process.

Also to be taken into account is the possibility of efficient control of corrosion in vacuum apparatus used in the second stage of evaporation (rapid-apparatus stage) by means of constructing shields for the cathode in heating chambers. At this point mention should be made of the fact that the use of copper heating chambers will be justified in the evaporation process used on alkalies.

Among the measures leading to the removal of residual salt from alkali after evaporation (and this should be in mind) is the method which employs a more prolonged settling of the alkali with simultaneous cooling. Concerning processes of chemical purification of alkali after evaporation, it can be said that the crystal hydrate method which has been used for a long time by industries abroad is not of interest to us since practice has shown it to be expensive because of the necessity of repeating the evaporation of alkali after the crystal hydrates have settled. Our problem is to adopt either the sulphate or the ammonium method. Preparations for research and experimentation necessary along this line should be a problem for our research workers. The question, however, is directly related to the amount of pure alkali which will be at our disposal as a result of the application of the mercury method. It is necessary to keep in mind that alkalies obtained from the soda-producing plants usually satisfy the requirements in the production of synthetic alkali, while alkalies derived from the mercury method not only offer a supply of a highly pure product but may be blended to enrich the corresponding alkalies obtained in diaphragm cells. As a result of this, perhaps there will be no need to purify lyes produced in diaphragm cells. The problem here consists merely in distributing alkali equally among the appropriate consumer groups.

In the field of selection, types of alkalies should be produced which would render them more readily feasible by the consumer. That is why, in addition to liquid and fused alkali, production of the commodity in flaky, lump, and powdered forms must be adopted in the future. Concerning the process of fusing alkali, it should be noted, however, that the scale on which the process is applied must be in strict accordance with actual demand for the fused product. Basically, supplying of liquid alkali should be organized and large-scale transport of liquid alkali in the newest types of tanks should be adopted in order to insure sufficient preservation of heat in the product during the journey so that the product remains in a liquid state during the entire time and will pour out of the tanks easily and quickly.

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Paralleling the method continuous fusion of alkali which is being advanced by some workers of the soda industry, the method which employs continuous production of either high-purity-fused or flaky alkali directly from the mercury cell decmders must be promoted in the chlorine industry.

For fusing iron-free alkalies, either nickel or nickel-lined boilers will have to be used.

In the realm of automatic machinery, equipment for automatic warning and automatic disconnection of cells must be available for the mercury method in case of disruptions in work of the mercury pumps and other disorders. Warning apparatus should be reliable. Simultaneous light and sound warning is best. Automatic warning is necessary in the event of changes in the concentrations of hydrogen in the chlorine and oxygen in the hydrogen. It would be of benefit to have on hand an automatic control for controlling the liquid level in tanks. The presence of automatic equipment for discovering grounding in cells is very important in electrolysis. The industry must be adequately equipped with different kinds of meters to calculate intermediate and main production output. Automatic machinery must be widely applied in the chlorine industry. This will insure great stability in the processes.

Aside from problems of a technical nature which have been examined above, we must pause over the problems of transporting chlorine products.

As liquid chlorine is used more widely, it will be necessary to devise a more modern method for transporting chlorine. The fact must be taken into account that we will probably deal with land, water, and air transport of liquid chlorine. Central base warehouses will be needed, as will filling, refilling, and distributing stations with suitable pump installations; tank cars; and river and ocean tankers. There will also be a need for appropriate personnel to maintain and supervise this vast economy.

The same conditions must obtain for supplying the national economy with other chlorine products (decomposers, disinfectants, etc.).

The conclusion should not be drawn from the foregoing, however, that the transportation of liquid chlorine is an independent goal.

The less chlorine leaving an enterprise in an unprocessed form and the more remaining within the chlorine enterprise for processing, the greater is the success of the chlorine industry. Combined production has great importance in the chlorine industry.

A considerable increase in the consumption [sic; probably production] of hydrochloric acid is also very important in order to satisfy the demands of new industries. Production of chloride derivatives of metals and metalloids (ferric chloride, aluminum chloride, silicon tetrachloride, titanium chloride, chlorine derivatives of phosphorus and antimony) may use up a considerable quantity of chlorine just as well-organized measures in the field of public health and purification of drinking and waste waters do. Estimates of chlorine to be used in the production of organic chlorine compounds were presented in S. Ya. Faynshteyn's article (Khim Prom, No 12, 1946).

In discussing the possibility of satisfying the chlorine demand, Ya. R. Gol'dshteyn's remark (Khim Prom, No 5, 1946) should be taken into consideration: "During the war more than a half of the plants of the Soviet Union's soda industry were located in the area occupied by the Germans." These plants are consequently being rebuilt. This means that the problem of the chlorine industry for the coming years consists in forcing somewhat the potential uses of chlorine to the extent that the amount of electrolytic alkali which would be obtained in the process would compensate us during the temporary decrease

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in the production capacity of the caustic soda plants.

Among the problems of a general and organizational nature, the most important is the problem of creating an atmosphere in the chlorine industry which would stimulate search for new ideas and would contribute to speedy and wide experimentation and adoptation of these ideas. Three groups of thinkers, the producers, the research workers, and the planners, participate in the introduction of new ideas. As experience has shown, direct cooperation of all three groups gives the best and quickest results. That is why the frequently noticeable separation, for example, of the research worker from the producer or the planner from the research worker and producer hampers the process of introducing new ideas. It is possible, for example, to have a plant at one place and the research and planning institutes at another. As a result, less would be accomplished than when the producer, research worker, and planner are set up within the plant. That is why a closer association of ideas and experiences of the producer, research worker, and constructor is expedient. Under such conditions there will be fewer distractions and more practical application. More suggestions and inventions will be made by designers, and the producer will not be in a position to have new ideas imposed upon him, but, on the contrary, he will be part designer and participant and interested in working out and formulating these new ideas.

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